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THE DETERMINATION OF MOLECULAR WEIGHTS.

By H. C. Biddle.

The influence of a dissolved substance upon the vapor-pressure of its solvent was a subject of study as early as the time of Gay-Lussac. The first generalization of much importance, however, was made by Wüllner[1] in 1858. This investigator showed that in aqueous solutions of non-volatile substances, the lowering of the vapor-pressure was roughly proportional to the quantity of substance dissolved. In the investigations of Wüllner and of those immediately following him, attention was directed largely to the study of salt solutions,[2] consequently more than a quarter of a century elapsed before a clear insight into the phenomena of vapor-tension was gained. The extension of the study of vapor-pressures to solutions other than aqueous, we owe chiefly to Raoult.[3] This investigator had noted the close relation existing between the diminution of the vapor-pressure of a solution, the lowering of its freezing-point, and the number of molecules of the dissolved substance, and was led by these considerations to study the vapor-pressures of ethereal solutions. His work gave definition to the entire subject, and is undoubtedly the most important that has ever been done on the vapor-tension of solutions.[4]

Among his results the following are of particular consequence: The relative vapor-pressure, $\frac{f'}{f}$, between 0° and 22° is independent of the temperature; the relative lowering of the vapor-pressure, $\frac{f-f'}{f}$, is proportional to the molecular concentration; the depression, $f-f'$, produced in a solution of a non-volatile substance, is independent of the nature of that substance; and the lowerings of vapor-pressure in various

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[1] Pogg. Ann., **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[2] Panchon: Compt. rend., **89**, 752 (1879); Tammann: Wied. Ann., **24**, 523 (1885); Emden; *Ibid*, **31**, 145 (1887); etc.

[3] Compt. rend., **103**, 1125 (1886).

[4] *Ibid.*, **104**, 976, 1430 (1887); **107**, 442 (1888). Ztschr. phys. Chem., **2**, 353 (1888). Ann. chim. phys., [6], **15**, 375 (1888).

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solvents are the same when in their solutions the ratio of the number of molecules of solute to that of the solvent is the same.

Raoult indicated the possibility of employing the lowering of the vapor-pressure of a solution in determining the molecular weight of a dissolved substance. In his opinion, however, the experimental difficulties were such as to give preference to the cryoscopic and ebullioscopic methods.[1] Both Tammann[2] and Raoult[3] have called attention to the possible errors in measuring vapor-pressure which arise from the presence of dissolved gases and from variations in surface concentration due to unequal evaporation or condensation.

Numerous attempts have been made to devise a ready and accurate method for measuring the vapor-pressure of a solution.[4] Raoult[5] and the most of the experimenters before him employed the barometric vacuum over mercury. Beckmann[6] undertook the study of such measurements with the avowed purpose of designing an apparatus which could be used practically in determining the molecular weight from the lowering of the vapor-pressure.

He had recourse to the static method and employed first of all a modification of the barometric vacuum. The difficulties encountered, however, led him to abandon this. A partially static method gave somewhat better results, but it likewise proved inferior to the ebullioscopic method, to which he thereafter directed his attention.[7]

Dynamical methods of measuring the vapor-tension have also been worked out with varying degrees of success. The essential feature of one of these, first suggested by Ostwald, consists in determining the relative lowering of the vapor-pressure from the ratio of loss of weight of solvent to gain in weight of an absorption bulb, when a slow current of air is passed, in order, through solution, solvent, and absorption bulb.[1]

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[1] Ztschr. phys. Chem., **2**, 372, 373.

[2] Wied. Ann., **32**, 683 (1887).

[3] Ztschr. phys. Chem., **2**, 359.

[4] Moser: Wied. Ann., **14**, 72 (1881); Bremer: Rec. trav. chim. Pays-Bas., **6**, 122 (1887); and others.

[5] Ztschr. phys. Chem., *loc. cit.*; Jour. de Phys., [2], **8**, 1 (1889).

[6] Ztschr. phys. Chem., **4**, 532 (1889).

[7] *Loc. cit.*

Kahlbaum[2] compares the static and dynamic methods and shows that both should yield like results.

Differential manometers of various forms for the direct measurement of differences in vapor-pressure have been suggested by Loeb,[3] Lord Kelvin,[4] Bleier and Kohn,[5] and others.

The following brief investigation was undertaken with the view of securing a serviceable apparatus for measuring, according to the static method, the difference in vapor-pressure between solution and solvent, and at the same time of simplifying the calculation of the molecular weight without introducing errors sufficiently large to vitiate the results.

As has been shown by Raoult, the lowering of the vapor-pressure of a solvent due to the presence of a non-volatile solute may be expressed by the well-known equation,

$$\frac{f-f'}{f}=\frac{n}{n+\mathrm{N}}.$$

When the concentration is low (not exceeding 7 molecules of solute to 100 molecules of solvent) there is equally applicable, as shown by the same investigator,[6] the expression

$$\frac{f-f'}{f}=\frac{n}{\mathrm{N}}.$$

Indeed this was the form first employed by Raoult in studying variations in vapor-tension.

In using the following apparatus there is no need that the molecular concentration should exceed that named. In these and similar determinations it is, consequently, much simpler to employ Raoult's second formula, $\frac{f-f'}{f}=\frac{n}{\mathrm{N}}$. We may regard as the "molecular depression" the diminution in vapor-tension of 100 grams of the solvent, produced by 1 gram molecular weight of substance dissolved in it. If we represent this constant by K and the number of grams of substance and of solvent by P and W, respectively, we readily obtain for a given solvent at a given temperature the equation,

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[1] Walker: Ztschr. phys. Chem., **2**, 602 (1888); Will and Bredig: Ber. d. chem. Ges., **22**, 1084 (1889); Orndorff and Carrell; J. phys. Chem., **1**, 753 (1897).

[2] Ztschr. phys. Chem., **6**, 594 (1890); **13**, 14 (1894).

[3] *Ibid.*, **2**, 606.

[4] Nature, **55**, 273, 295 (1897).

[5] Monatsh. Chem., **20**, 505, 909 (1899).

[6] Compt. rend., **104**, 976.

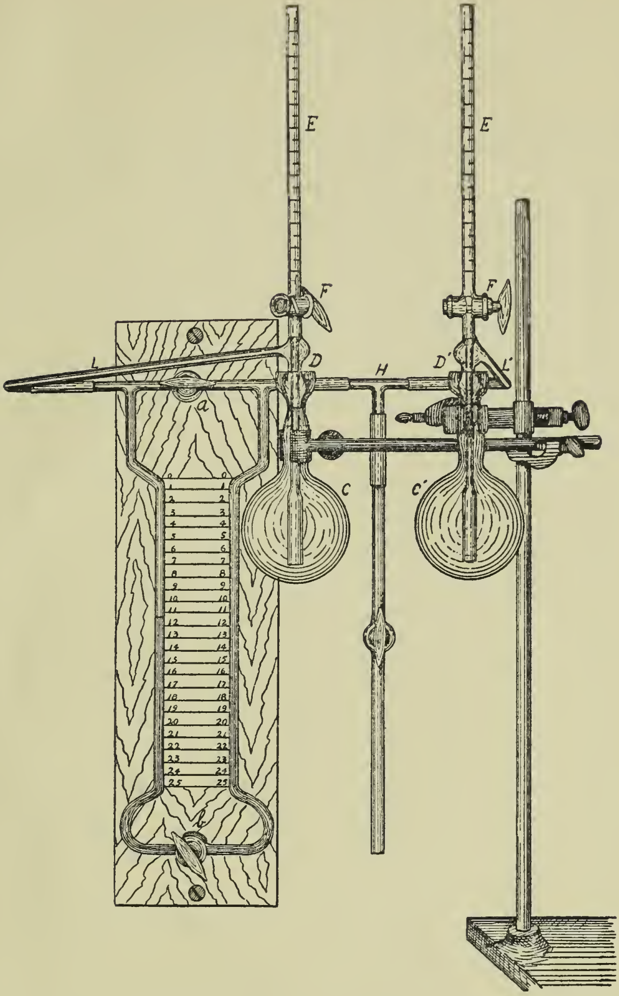
$$M = K \frac{100}{f - f'} \cdot \frac{P}{W}.$$

This expression, which, as we see, is identical with that for the boiling-point apparatus of Beckmann, renders it unnecessary to ascertain the direct vapor-pressure of either solution, or solvent.

The apparatus used is adapted to measure directly the lowering of the vapor-pressure, $f - f'$. A differential manometer with an inner diameter of 4 mm. is provided with two glass stop-cocks, *a* and *b*. The flasks, *C* and *C'*, into which, respectively, solution and solvent are introduced, are of nearly the same capacity (about 250 cc. each). The capillary tubes *L L'* connecting the flasks with the manometer are of equal length and form one piece with the ground-glass stoppers *D D'*.

The attachment between capillary tubes and manometer is made with heavy-walled rubber tubing. Tubes *E E'*, with glass stop-cocks at *F F'*, pass through the stoppers to within 1 to 2 cm. of the bottom of the flasks. The upper portions of these tubes are graduated to 0.1 cc. and should have a capacity of 10 to 15 cc. To insure against leakage, the ground-glass connections *D D'* are further sealed with mercury. A T at point *H* permits a ready exhaustion of the apparatus.

In conducting a determination, the flasks are held at a fixed temperature by immersion in a suitable thermostat. Stop-cock *a* is then opened, *b* closed, and the apparatus partially exhausted. Equilibrium is determined by the constancy of the manometric fluid when *b* is opened and *a* closed. Both stop-cocks of the manometer are now closed and into each flask, respectively, is introduced an equal volume of solution and solvent. After a few minutes *b* is opened and the reading taken when the height of the manometric fluid has become constant. Olive oil was used in the manometer, and this was



chosen chiefly because of its low vapor-tension. With a reduction of the internal pressure to about 300 mm. of mercury, equilibrium is usually attained in fifteen to twenty minutes.

In measuring vapor-pressures the increased concentration of the solution due to the partial evaporation of the solvent, will lead, as Raoult[1] has indicated, to erroneous results, if no correction be made for this error. In the above apparatus this source of error is rendered negligible in the calculation by the introduction of a sufficient quantity of the solution (10 to 15 cc.).

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[1] **Ztschr. phys. Chem.**, *loc. cit.*

As already noted, inaccuracies arise in such determinations from surface concentration.[1] This difficulty is obviated in the present case by the large surface of the liquid and by slightly agitating the flask. There was further indicated the necessity of eliminating from solution and solvent, when measuring their vapor-pressure, all foreign volatile substances such as gases. As may be readily seen, this source of error is negligible in the apparatus considered, provided only that the gaseous content of solution and solvent is the same. With this end in view, both liquids are introduced under as nearly as possible the same conditions of temperature and pressure. The slight difference in air-solubility naturally subsisting between solution and solvent is here ignored.

In the change of position of the manometric liquid, the equilibrium of the air-content of the two flasks is slightly disturbed. This will invariably render the observed difference in vapor-pressure less than that actually existing. The error here introduced, however, is proportional to the observed difference and consequently disappears in the constant K when this latter is experimentally determined.

The slight contamination of the liquids introduced by vaseline or similar lubricant on the stop-cocks $F F'$, might be considered as a source of error, but the results obtained indicate that this may be disregarded.

The solvent used in any case should not have a vapor-pressure much less than 225 mm. of mercury. Consequently, in employing liquids of lower vapor-pressure, it is better to work at a correspondingly higher temperature.

It was found that invariably the most satisfactory results were obtained by taking the mean of two determinations, the solution and the solvent in the two cases being interchanged between the two flasks. Each of the following readings represents the mean of two such determinations.

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[1] Tammann and Raoult: *Loc. cit.*

The ether and carbon bisulphide used were carefully purified, the former being distilled over sodium.

Temperature variations in the thermostat were held within 0°.15 C.

The pressure was reduced to 295–305 mm. and into each flask were introduced 10 cc. of liquid.

TABLE I.

Solvent, ether; K = 260.00; Temperature, 15°.

Naphthalene.

$\frac{P}{W}$.	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.0639	13.3	124.9	128
"	13.0	127.8	"
0.06565	13.3	128.4	"
"	13.33	128.0	"
0.0689	13.85	132.3	"
"	13.94	128.5	"
"	14.0	128.0	"

Cinnamic Acid.

$\frac{P}{W}$.	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.05922	10.25	150.2	148
0.06716	11.65	149.9	"
"	12.0	145.5	"

Salicylic Acid.

$\frac{P}{W}$.	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.06549	12.4	137.3	138
"	13.0	131.0	"
"	12.6	135.1	"

Iodine.

$\frac{P}{W}$.	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.07139	7.4	250.8	254
"	7.5	247.5	"
"	7.3	254.2	"
"	7.4	250.8	"

Solvent, carbon bisulphide; K = 171.50: Temperature, 15°.

Naphthalene.

$\frac{P}{W}$.	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.0851	11.0	132.7	128
"	11.2	130.3	"
0.07348	9.9	127.3	"
"	9.7	129.9	"

Phenanthrene.

$\frac{P}{W}$.	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.06025	6.05	170.8	178
0.06971	7.05	169.6	"
"	7.00	170.8	"

Sulphur.

0.07435	4.9	260.2	256
"	"	"	"

Phosphorus.

0.07881	10.45	129.3	124
"	10.3	131.2	"

Iodine.

0.08115	5.5	253.0	254
"	5.8	240.0	"
"	5.4	257.8	"

The molecular weight of iodine as above determined is of some interest in view of the speculation that has obtained regarding the molecular aggregation of the element in different solvents. As is well known, iodine dissolves in some liquids as carbon bisulphide and the hydrocarbons with a violet color, in still others as alcohol, ether, and other alcoholic derivatives with a brownish-yellow color. Other solvents again yield intermediate gradations of color. It was early inferred that the color differences were due to a difference in molecular aggregation, and some of the experimental data seemed to favor this conclusion. Wiedemann[1] called attention to the fact that the solution in carbon bisulphide, when cooled with carbon dioxide and ether, became brownish-red. This result, doubted by Arctowsky,[2] was later confirmed by Krüss and Thiele.[3] On the other hand, brown solutions in the esters of the fatty acids become violet on warming to 80° C. Gautier and Charpy[4] for a time thought that they had discovered a difference in chemical behavior between violet and brown solutions.

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[1] Wied. Ann., **269**, 580 (1888).

[2] Ztschr. anorg. Chem., **6**, 403 (1894).

[3] *Ibid.*, **7**, 70 (1894).

[4] Compt. rend., **111**, 645 (1890); Compare Beckmann and Stock: Ztschr. phys. Chem., **17**, 130 (1895).

The difference in the absorption spectra of variously colored solutions was also advanced as indicating a difference in molecular complexity.[1]

An attempt was made by Loeb,[2] working under Ostwald, to determine the molecular condition of iodine in solution from the change in vapor-pressure of the volatile solvent. His results led him to believe that in ether the molecule is I_4, while in carbon bisulphide it lies between I_2 and I_3. His method, however, was difficult to carry out, and ignored several of the sources of error already considered.

The careful work of Beckmann,[3] Nernst,[4] Krüss and Thiele,[5] and others,[6] has, however, shown conclusively that the molecule of iodine in the different solvents studied is diatomic, irrespective of the color of the solution.

Alcohol, as a solvent, does not readily lend itself to the determination of the molecular weight of iodine. Of the two methods commonly employed in such determinations, one is inapplicable because of the low freezing-point of the solvent, and the other appears to be somewhat unreliable because of the action of the element on boiling alcohol.[7] At the same time it may be noted that fairly concordant results have been obtained by the latter method.[8] The vapor-tension of alcohol at 15° to 20° is insufficient to afford trustworthy data by employing at those temperatures the apparatus described in this paper.

In connection with the results as tabulated above, an attempt was made to measure the osmotic pressure of a solution of iodine in alcohol.

The first exact quantitative measurements of osmotic pressure we owe to the painstaking work of Pfeffer.[9] He employed aqueous solutions and showed very clearly in such

[1] Compt. rend., **110**, 189; Rigollot: *Ibid.*, **112**, 38 (1891).

[2] Ztschr. phys. Chem., **2**, 606.

[3] *Ibid.*, **5**, 76 (1889); **17**, 107 (1895).

[4] *Ibid.*, **6**, 16 (1890).

[5] Ztschr. anorg. Chem., **7**, 52 (1894).

[6] Hertz: Ztschr. phys. Chem., **6**, 358 (1890).

[7] Krüss and Thiele: Ztschr. anorg. Chem., **7**, 61.

[8] Beckmann and Stock: Ztschr. phys. Chem., **17**, 117.

[9] Osmotische Untersuchungen, Leipzig, 1877.

cases the close relation between the osmotic pressure and the molecular concentration of the dissolved substance.

Since Pfeffer's work but little advance has been made in the methods of measuring osmotic pressure, although recently Morse and Frazer[1] have prepared a cell which seems to be particularly well adapted for recording high pressures. Aside from indirect determinations, however, such as those which may be derived from the boiling- or freezing-point methods or from the method suggested by Noyes and Abbott,[2] apparently no attempt has yet been made to measure directly the osmotic pressure of solutions other than aqueous.

In the following measurements a slight modification of Pfeffer's apparatus was used. It was found to be a comparatively simple matter to obtain serviceable cells in aqueous solutions, but the successful employment of these cells in alcoholic solutions proved somewhat difficult. The results obtained, however, point conclusively to the diatomic condition of iodine in the solvent and confirm the ebullioscopic determinations of Beckmann and Stock.[3]

A porous clay cell of about 25 cc. capacity was treated successively with dilute potassium hydroxide and hydrochloric acid (about 3 per cent), and was finally well washed with distilled water. Into the neck of the cell was then sealed securely with Portland cement a glass T. As soon as the cement had hardened, the cell was thoroughly injected with water and a membrane of copper ferrocyanide deposited according to the method employed by Pfeffer. A semi-permeable membrane was formed in this way, which would readily support a pressure of 1 atmosphere. The cell thus prepared was freed from soluble salts by prolonged treatment with distilled water. It was then transferred through water-alcohol of gradually increasing alcoholic strength to the ordinary 95 per cent alcohol.

An open manometer, with a capillary tube of 1.5 mm. inner diameter, was used to record the pressure. Variation in the concentration of the solution due to interaction of the iodine and the mercury of the manometer extended only a few centimeters along the capillary above the surface of the mercury. The cell was closed and connected with the manometer by ordinary well-fitted corks, which were sealed externally to the glass T to preclude possibility of slipping.

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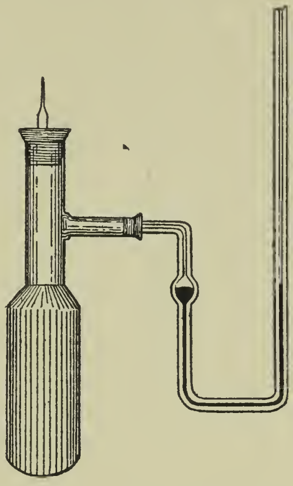
[1] This Journal, **26**, 80 (1901); **28**, 1 (1902).

[2] Ztschr. phys. Chem., **23**, 56 (1897); also Goodwin and Burgess: Phys. Rev., **7**, 171 (1898).

[3] *Loc. cit.*



The use of copper ferrocyanide as a membrane with iodine is not, as might be supposed, open to objection because of the oxidizing influence of the latter. While chlorine and bromine act upon this salt immediately, it is unaffected, at the ordinary temperature, after an hour's contact with an alcoholic solution of iodine such as was used in these determinations.[1]

The rise of the mercury in the manometer was much more rapid with alcoholic than it was with aqueous solutions of corresponding molecular concentration. The maximum pressure was attained in sixty to seventy-five minutes, and this pressure remained constant for nearly the same length of time. The molecular weight was calculated from the expression,

$$M = 22.4 \times 760 \times (1 + \alpha t)\frac{R}{P},$$

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[1] That no change had occurred was shown by filtering and titrating the filtrate in the usual way with a solution of thiosulphate.

where M is the molecular weight, R the amount of substance dissolved in 1 liter of the solution, and P the osmotic pressure expressed in mm. of mercury.

TABLE II.

R.	Temperature.	P.	Molecular weight found.	Molecular weight calculated.
3.98	12°	265.1	266.8	254
4.14	17°	260.3	287.6	"
4.14	17°	277.8	269.5	"

In the above measurements of osmotic pressure I have been assisted by Miss Myra Winn, and in those of vapor-pressure by Mr. M. L. Chappell, and I take this occasion to express my appreciation of their earnest and careful work.

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